Capillary Closed Tube Analysis

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Synopsis

We applied closed tube analysis to some minerals, using thin walled glass capillaries in place of tubes of ordinary dimension, samples being placed in the capillaries, alone or together with fluxes—KCN, iodide mixture or hypophosphites. The last fluxes were best available for easy detection of various metals owing to its reducing and coloring reaction.

I. Introduction

Closed tube analysis, which, as one of the dry method analyses, has remained within the confines of preliminary analysis as yet, was intended by us further for the detection of metallic elements.

In closed tube analysis heretofore samples used were not powdered but in small mass, because if powdered sample was made to put into the tube, more or less it might stick to its wall, preventing, there may be much fear, the sublimate from clear observation. We put a very small amount of a sample into the capillary and closed the mouth where the sample was introduced. This mouth being placed downwards so as to be the bottom of the capillary made possible the use of powder samples. A capillary is easy to be treated under a microscope and so the inside of it, changed by heating, can be set for careful examinations.

Next we tried to heat samples mixed with flux, a device which had not yet been made.

First KCN was employed as reducing reagent and iodide mixture for coloring the products, but this was found not satisfactory for the detection of metallic elements. If there be any flux having such reducing power as KCN has and in addition giving respective proper colors to respective metallic elements, it would be a great convenience. In 1941 Valkenburgh[1] reported that he made experiments in which fused masses of U, V, Co, Cr, Mo, W, Mn, Ti, Te were colored when he fused them in evaporating dishes with ammonium hypophosphite. With this hypophosphite as flux we made, in closed capillaries, analyses of some milligrams of pure chemical substances and succeeded in detecting Hg, Se, As, Cd, Cu, Ag etc. as well as those elements mentioned above.[1] Then applications were made to several kinds of minerals.

II. Experimental procedure

A glass tube of 15 to 20 mm in diameter is elongated into a capillary with about

(1) H. B. v. Valkenburgh and T. C. Crawford, Ind. Eng. Chem., Anal. Ed., 13, (1941), 459.

1 mm of caliber and about 0.1 mm of wallthickness, of which about 10 cm is cut off for use. Being perpendicularly pressed by this capillary, a sample, which has been placed on a porcelain plate, is let in the capillary, filling about 5 mm from the mouth. The sample introduced is roughly a few milligrams, which is pushed further into it with a slender glass rod so as to be placed at 3 to 5 mm from the mouth. The end of the capillary is sealed, care being taken to heat the sample as little as possible. This sealed end is heated by a small flame of a microburner or a Bunsen burner. Then the changed states of the sample and the inside of the capillary are fully examined under a microscope.

III. Experimental results

(1) Cases where fluxes are not used

When a sample, placed alone in a capillary, is heated, it is sometimes decomposed and produces gas and/or sublimate. Gas evolved is detected by the usual method; only as to oxygen the following way was adopted. Carbon powder is thinly attached to the inside wall of the capillary near its mouth. And at the same time when the sample is heated at the sealed end, this carbon powder is also heated at the other end. If oxygen is evolved from the sample the carbon burns. As the gas evolved from a solid when heated can hardly be macroscopically observed, we added KCl to the sample before heating. The gas, if produced, was seen going up in the transparent melt of KCl. From the crystal forms of sublimates a microscope of 200 magnifications could detect As_2O_3, SeO_2 and I_2. The ordinary classification of sublimates, based only upon colors, (white, yellow, red, grey, black) was not available for the purpose of element detection. This is not the case with our experiments by using capillaries. We cut off the part where the sublimate lay in a girdle, in which put Na_2CO_3 (or Na_2SO_3 when Se) and then reclosed the cut end of the tube, heating it again. Thus we succeeded in detecting elements from Hg-, As-, Se-compounds, that is, Hg beads, arsenic-mirror, and red Se. The difficulty in determining whether yellowish oily droplets are of sulphur or of phosphorus is removed by putting a small quantity of $KClO_3$ into the capillary, both ends sealed, and heating it with a weak flame. The droplets of sulphur will be burned away, while those of yellow phosphorus make a film of red phosphorus all over the inner surface of the wall of the capillary.

(2) Cases where fluxes are used

Samples, with KCN mixed as reducing reagent, were placed in closed tubes and heated. This agent reduced many heavy metal compounds to metallic elements, but by this way it was difficult to differentiate those elements. For the purpose of coloring them and making them easy to sublimate, we employed, as a flux, an iodide mixture, a mixture of $KHSO_4$ and KI in equal quantities. The results were that Se, As, Hg made colored sublimates and Sn, Sb, Pb, Bi etc. colored fused masses. The latter, however, were, many of them, of similar color to one another leading to the difficulty of respective identifications. Therefore it was desired that

we should have such an agent as would make both reducing and coloring reactions possible at the same time, and so detection of respective elements easy. After the method Valkenburgh adopted, we tried closed tube analyses by using capillaries. Generally, hypophosphites[2] are a powerful reducing reagent, which, when heated, produces H_2 and PH_3, and is decomposed as follows:

$$5KH_2PO_2 = KPO_3 + K_4P_2O_7 + 3PH_3 + 2H_2$$
$$13Ba(H_2PO_2)_2 = 6Ba_2P_2O_7 + Ba(PO_3)_2 + 12PH_3 + 4H_2 + 4H_2O$$

The phosphorus compounds thus decomposed are most suitable as coloring matter. Ammonium hypophosphite evolves NH_3 gas which blows off the sample from its original position, potassium or barium hypophosphite was more suitable. Samples employed in our pilot experiments were chemically pure chlorides, sulphates, sulphides and oxides.

According to the results of our pilot experiments, compounds of Se, Te, Hg, Cd and As are reduced to respective elements in the state of sublimate.

Te-compounds are reduced to metallic tellurium, making a grey film of sublimate girdle near the sample. A microscopic observation told that the girdle is composed of metallic beads.

Cutting the capillary at a part between the sample and its sublimate, to the latter, adding a small amount of concentrated sulphuric acid, and then heating the capillary, we had the girdle changed to reddish purple color. Further heating turned it into a white solid, and if continued, to yellowish white oily droplets.

Cd-compounds are also of grey beads in their sublimate girdle as seen under a microscope, but do not change to reddish purple color, by the treatment of H_2SO_4.

U, V, Cr, Co, Ti, Cu, Mn, Ag take on respective characteristic colors in their fused masses, though not producing any sublimates.

U-, V-, Cr- compounds give green masses, as given by Valkenburgh.

Mn-compounds give white masses, this is also just the same as his result, the white fused mass shows reddish violet, color of MnO'_4, when heated with HNO_3.

Co-compounds give bluish purple, coloring to the inside of the glass tube.

Ti-compounds also show a blue color and are often seen crystallized under the microscope.

Ag-compounds produce silver-white beads, which can be observed under a microscope. When the sample is kept being heated, macroscopically observable silver-white metal beads are produced, the glass tube colored in yellowish brown.

Cu-compounds take a reddish black color, but light red at the closed part of the capillary. This fused mass, when cut at its middle and added with $KClO_3$, becomes blue on heating.

Other heavy metals show colors too similar for exact detection.

But among them Bi-compounds which are liable to reduction, can be seen under a microscope producing numerous metal beads like Hg beads, but are not sublimating, and Sb-compounds also are seen to produce grey-black beads through a micro-

(2) C. Rammelsberg, J. Chem. Soc., 26, (1873), 1.

scope. After adding HNO_3 and observing the compound again under a microscope, we find black beads surrounded by white meta-antimonic acid.

What have been stated above are our experiments with pure chemical substances. Next we shall refer to our application to the crude TeO_2 and mercuric telluride.

When the crude TeO_2 is heated in a capillary without any flux added, a red sublimate is produced, here there being no girdle made; while, the sample mixed with barium hypophosphite, heated, produces red and black sublimates near itself. These sublimates heated slightly, the red sublimate is moved to the middle of the tube, the black one remaining where it is. This is a group of black beads, which are cut and put to H_2SO_4 treatment for Te-identification.

On heating mercuric telluride with barium hypophosphite, a girdle of black sublimate is obtained. A little heating of this girdle divides easily sublimable part from the residue; the former moving towards the middle of the capillary. This is known to be Hg beads by microscopic observation, and the other greyblack metal beads of tellurium, which is cut off and identified by the above method.

(3) Application to minerals

We made applications of this method of closed tube analysis by aid of barium hypophosphite or potassium hypophosphite as a flux to several kinds of minerals.

Realgar (As_2S_3) produces black sublimate, which is found to be arsenic-mirror under a microscpoe.

Cinnabar (HgS) produces black sublimate, which is identified as Hg beads under a microscope.

Proustite (Ag_3AsS_3) gives black sublimate and arsenic-mirror. In the heated sample are discovered a lot of silver white beads by a microscope, which, after further heating, can be seen with naked eyes. The coloring of the capillary in yellowish brown seems to be an evidence of the presence of Ag.

Luzonite (Cu_3AsS_4). The sample becomes reddish black, making arsenic-mirror in the upper portion of the tube. If the part containing the sample is cut at the middle, added with $KClO_3$ and heated, it changes blue.

Smaltite ($Co(Ni)As_2$) produces arsenic-mirror in the middle of the tube, the sample acquiring bluish violet color, the glass too colored blue partly.

Pyrolusite (MnO_2), the fused mass takes first white color, then becomes transparent. When heat with a droplet of HNO_3, it shows the presence of MnO'_4-reddish purple color.

Chromite ($FeO{\cdot}Cr_2O_3$), dark green fused mass is obtained. Fusing it with Na_2CO_3 and adding a drop of HNO_3, it becomes yellow.

Rammelsbergite (main components – Ni, As, Bi, S). Besides arsenic-mirror, many fine metal beads are observed in the fused part under a microscope. This is in many cases so with Bi compounds.

Summary

We have studied closed tube analyses employing capillaries, first without, then with flux-KCN, iodide mixture and hypophosphites. The best result was obtained when hypophosphites were used. That is, Se, Te, As, Hg and Cd were sublimated as elements from their compounds, well identified, and U, V, Cr, Co, Ti, Mn, Cu and Ag were changed into colored melts, easily detected.

Further we gave several applications of this method to the analysis of various kinds of mineral matters.

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